GEORGIA INSTITUTE OF TECHNOLOGY — OFFICE OF CONTRACT ADMINISTRATION

PROJECT ADMINISTRATION DATA SHEET

[X] ORIGINAL [ ] REVISION NO. _____

Project No. G-33-648 (R-5985-0A0) GTRC/~~GIT~~ DATE 7 / 16 / 85

Project Director: Dr. P. Sturrock School/~~Dept~~ Chemistry

Sponsor: Aluminum Co. of America
Alcoa, Tennessee

Type Agreement: Research Project Agreement G-33-648/P.O. CE395960AT

Award Period: From 7/1/85 To 6/30/86 (Performance) _____ (Reports)

Sponsor Amount:	This Change	Total to Date
Estimated:	$	$
Funded:	$ 28,993 I.P.R. $2,999*	$ 28,993

Cost Sharing Amount: $ N/A Cost Sharing No: N/A

Title: Determination of Silver in Aluminum by Square-Wave Anodic-Stripping Voltammetry

ADMINISTRATIVE DATA OCA Contact Ralph Grede x-4820

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2) Sponsor Admin/Contractual Matters:

Defense Priority Rating: N/A Military Security Classification: N/A

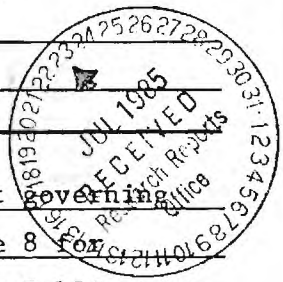
(or) Company/Industrial Proprietary: ~~See Paragraph 10~~

RESTRICTIONS

See Attached N/A Supplemental Information Sheet for Additional Requirements.

Travel: Foreign travel must have prior approval – Contact OCA in each case. Domestic travel requires sponsor approval where total will exceed greater of $500 or 125% of approved proposal budget category.

Equipment: Title vests with No equipment proposed.



COMMENTS:

Research Agreement is dated 7/1/85 and is used as the primary instrument governing this project. See Article 10 for Publication Restrictions: See Article 8 for Reporting Requirements: Patent Rights Paragraph 12*: Consideration for Publication and Restriction Rights -- see Par. 11 -- is $2,999.

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SR913

SPONSORED PROJECT TERMINATION/CLOSEOUT SHEET

Date 9/18/86

Project No. G-33-648 School/~~Lab~~ Chem.

Includes Subproject No.(s) N/A

Project Director(s) P. E. Sturrock GTRC / ~~GIT~~

Sponsor Aluminum Co. of America

Title Determination of Silver in Aluminum by Square-Wave Anodic-Stripping Voltammetry

Effective Completion Date: 6/30/86 (Performance) _____ (Reports)

Grant/Contract Closeout Actions Remaining:

- [ ] None
- [XX] Final Invoice or Final Fiscal Report
- [ ] Closing Documents
- [ ] Final Report of Inventions
- [ ] Govt. Property Inventory & Related Certificate
- [ ] Classified Material Certificate
- [ ] Other _____

Continues Project No. _____ Continued by Project No. _____

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FORM OCA 69.285

G-33-648 Final Report - DRAFT Copy

ANODIC STRIPPING ANALYSIS FOR SILVER IN ALUMINUM

by

Peter E. Sturrock

School of Chemistry

Georgia Institute of Technology

INTRODUCTION

The contract between Alcoa and the Georgia Institute of Technology was signed in July 1985 and work was started immediately. At various times, progress in a particular direction was found to be unsatisfactory and new directions were devised and followed. The discussion below is divided into four phases dealing with four types of experiments. As the end of the first year approached, the Principal Investigator (PI) recognized that the results achieved at that time were inadequate and the work was continued by Georgia Tech for an additional quarter with no additional expense to Alcoa. Now, the results achieved are very close to those desired originally and the final portion of this report suggests an outline for a possible continuation of this research project.

The ultimate objective of this research project is the development of a method to determine current efficiency in a Hall cell. Alcoa has suggested that some silver (e.g. about a pound) be added to the aluminum pad in a Hall cell and that the concentration of silver in the pad be monitored with time to allow calculation of the production of aluminum. Alcoa estimated that this procedure would require an analytical determination with a precision of 0.1%. Previous attempts, using emission spectroscopy, did not have adequate precision. The PI suggested that anodic stripping voltammetry would have adequate sensitivity and selectivity to deal with the estimated 50,000:1 mole ratio of aluminum to silver

and, if properly automated, might have adequate precision. This was the basis of the contract which had the first-year goal of demonstrating feasibility.

PHASE I: ELECTROCHEMISTRY IN BULK SOLUTION

When the project started, the flow cell to be used on the project had not arrived. Therefore, it was decided to develop the new computer programs and do a series of experiments in bulk solution. The programming was finished with minimal problems, but experiments in bulk solution quickly demonstrated that reproducibility could not be achieved in either stirred or unstirred bulk solution. This is attributed to the need for absolute reproducibility of both the solution around the electrode and the condition of the surface of the electrode. The use of mercury electrodes would have resulted in much more reproducibility in the system, but the low oxidation potential of mercury, compared to silver, made this approach out of the question.

PHASE II: INITIAL FLOW-CELL EXPERIMENTS

Upon receipt of the flow cell from Hewlett Packard (a prototype provided at no cost) flow experiments were initiated. Reproducibility was improved over the bulk-solution experiments, but was still unsatisfactory, and the sensitivity was disappointing. The largest volume injector loop on hand contained 0.1 mL. While a larger volume loop seemed to be the answer for the sensitivity problem, such a loop would have a very large ratio of surface area to volume and would result in a long tail on the injection bolus. Such a tailing bolus would be very detrimental to the experiment because a relatively long washout time would be required between repeat injections and the reproducibility in filling such a loop is questionable.

After discussions with several experts and with representatives of the injector manufacturer (Valco), the PI concluded that it would be necessary to replace the injector valve with one made for 1/8th inch tubing instead of the 1/16th inch tubing which is now standard. This would allow use of loops made from 1/8th inch tubing and result in a much more favorable ratio of volume to surface area. In addition, it was decided that a rapid switching of the injector valve, under computer control, would allow reproducible partial-loop injections which would have an almost ideal shape for the bolus, resulting in greatly improved reproducibility and a much higher repetition rate. To implement this revised approach, Alcoa ordered the new injector while Georgia Tech ordered the air actuator and the high-speed switching accessory. An existing computer interface was used to control the high-speed switching accessory and the PI generated new versions of the control program to provide the timed operation of the valve.

While awaiting procurement action on the new injector, work continued without any injector. Silver was added to the reservoir for the carrier stream. It was soon discovered that the Spectra-Physics SP8770 pump had sufficient flow pulsations as to result in sweep-to-sweep variations although reproducibility in the 1-2% range was obtained. It was also recognized that in the long run it would be necessary to control the temperature by enclosing the apparatus in a thermostated cabinet.

In an attempt to avoid the flow pulsations from the pump, the SP8770 was replaced by a Haskel pneumatic-amplifier pump. It was found that the silver in the carrier stream was being reduced by metals in the cylinder of the Haskel pump. Two different Haskel pumps were tried, as well as a pulse dampener with the SP8770, but it was necessary to wait for the new injector valve to arrive before meaningful experiments could proceed.

PHASE III: THE NEW INJECTION VALVE

The installation of the new injection valve, with the increased injection volume, resulted in a great increase in sensitivity. Unfortunately, reproducibility was very poor and a series of abortive attempts to identify the problem began. Because of the experience with the silver reduction inside the Haskel pump, the metal of the injector loop and fill port was suspected of reducing the silver. The stainless-steel loops that came with the new valve were replaced with loops fabricated from Teflon coated steel tubing. In addition, the entire loop-filling operation was automated and teflon tubing used to connect the sample pickup point to the injector. The loop is now filled by suction from a vacuum chamber with a solenoid valve between the chamber and the injector valve. (see Figure 1.) The solenoid valve is controlled by the computer so that sample solution is pulled through the loop for a carefully timed interval while the electrode is being cleaned at an extreme anodic potential.

After these changes, short-term reproducibility improved. Often, ten or so repeats could be recorded with good reproducibility, but then a sudden change in the response would occur and set-to-set reproducibility was still poor. These changes could be correlated sometimes with apparent changes in flow rate. The problem was that the Haskel pump is a pressure-controlled pump and there is no flow meter available to measure flow in the range of 1 mL/minute. It was clear that uncontrolled changes in flow rate were resulting in changes in response. At this time, a rough parameter optimization was performed. Also, copper was tested for possible interference with negative results.

PHASE IV: THE SYRINGE PUMP

After discussions between Alcoa and Georgia Tech, it was concluded that the only hope of meeting the goals of the project was to try a different type of pump. Alcoa arranged for the delivery of a demonstrator pump from ISCO and this syringe pump has been used for the final phase of the work. When the pump arrived, the pressure-transducer preamplifier housing had come loose from its anchor point, the pressure gauge was inoperative, and there was no instruction manual. However, ISCO mailed a new manual to Georgia Tech and Georgia Tech repaired the pump and put it into operation.

It was immediately found that small particles in the flow stream were causing partial blockages of the capillary tubing which serves as the inlet jet of the wall-jet cell. Since the ISCO syringe pump is a flow-volume controlled pump, in contrast to the pressure-controlled Haskel pump, the partial blockages could be identified by changes of pressure in the system. The next step was to find the source of the particles. Both the carrier stream and the sample solution were filtered before reaching the injector. The possibility of a precipitation reaction on mixing the solutions was considered. However, it was found that particulates resulted even when the injector was operated with carrier solution in both the sample line and the carrier-stream line. It now seems that the particles are fragments from the plastic-coated rotor of the injector. This will be confirmed by analysis of the particles. In the meantime, an inline filter has been installed between the injector valve and the cell and a much more regular flow has resulted in much improved reproducibility of response.

PRESENT STATUS

The apparatus is depicted in Figure 1 and a set of replicate sweeps is

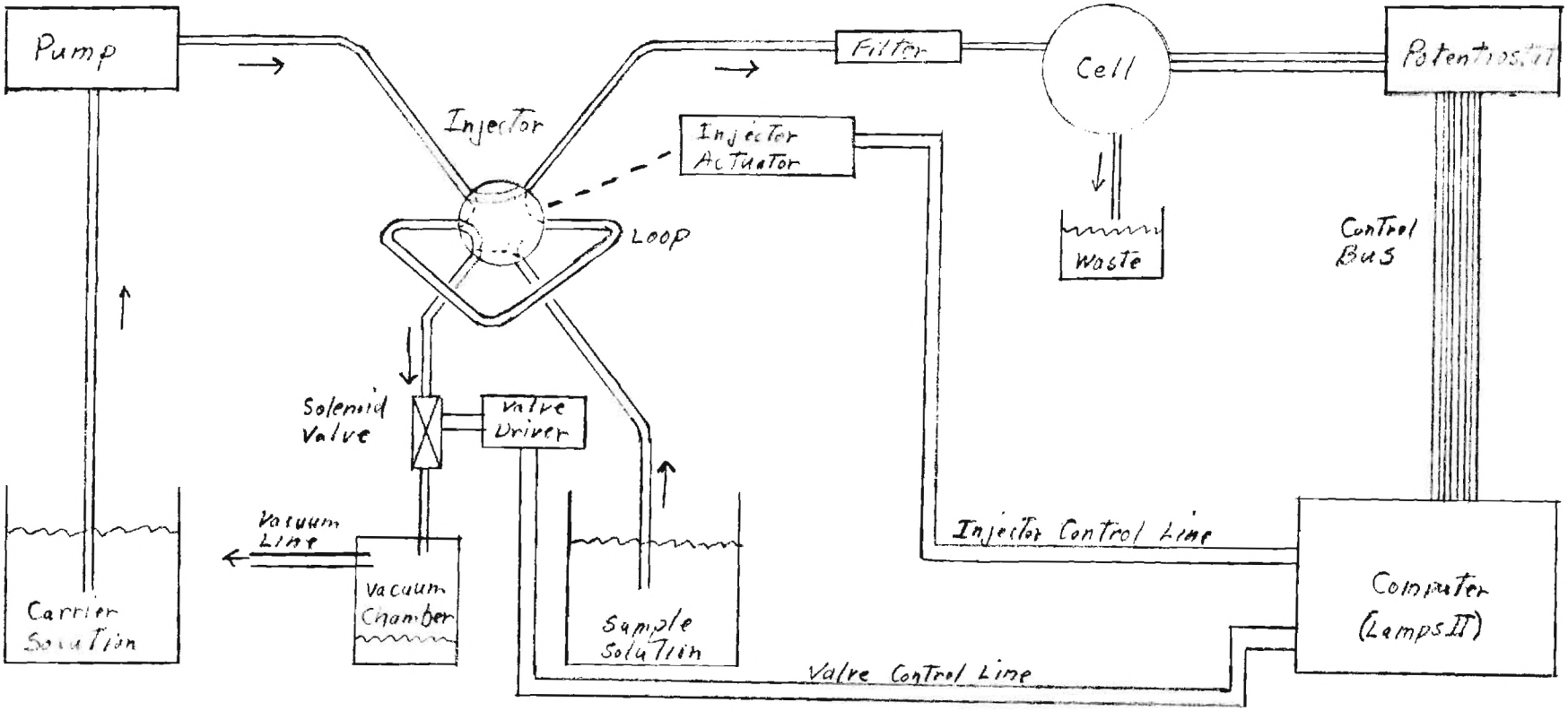

Figure I. Block diagram of instrumentation.

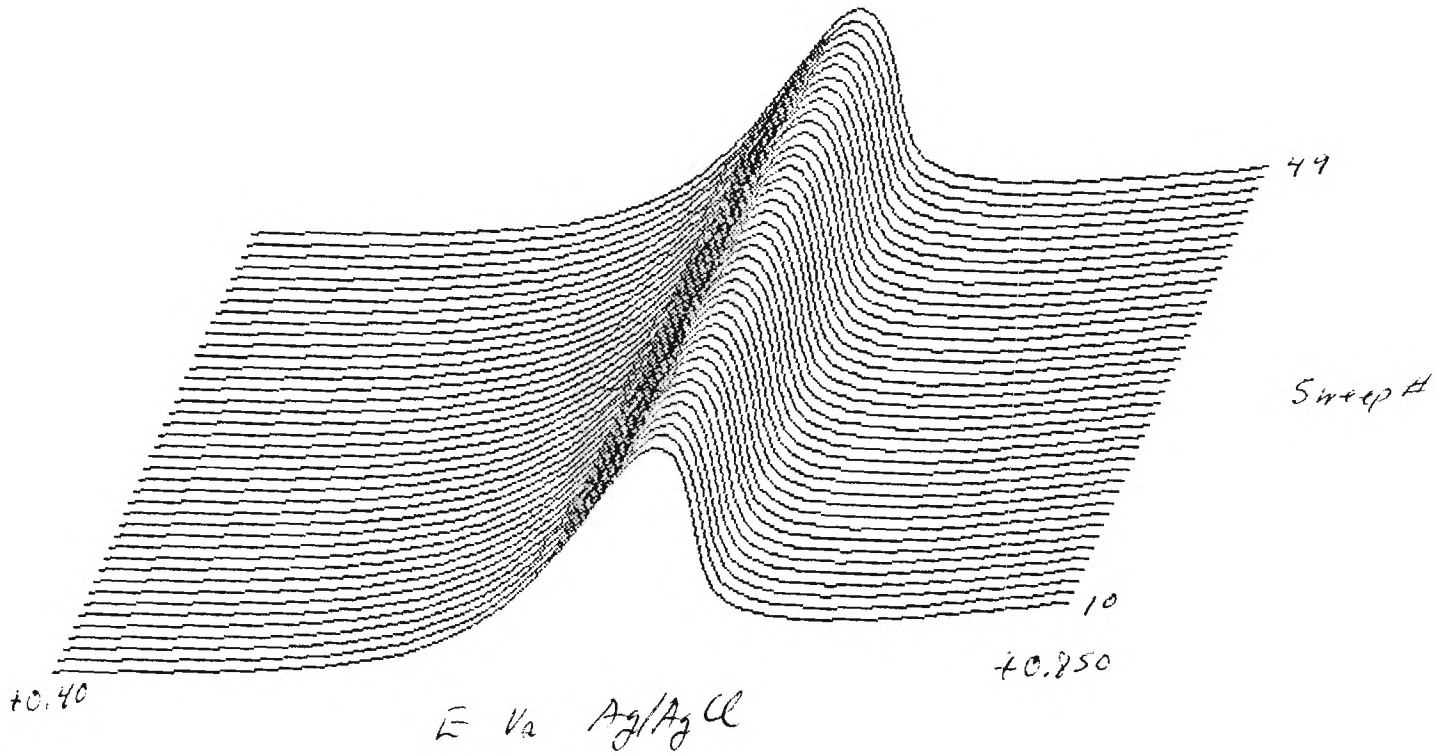

Figure 2. Sweeps 10 through 49 of run FR8. Solution is 5×10^{-6} M $AgNO_3$ in 0.1 M $Al(NO_3)_3$. Flow rate is 3.0 ml/min. Repetition Time is 38 seconds.

shown in Figure 2. During the final sets of experiments, numerous series of repeats were obtained with standard errors around 0.2%. Seldom was the standard error greater than 0.5% and in several runs the standard error was between 0.1 and 0.2%. These experiments used a sample solution of 5.0×10^{-6} molar silver nitrate in 0.10 molar aluminum nitrate. In most cases the response was found to increase or decrease in an approximately linear manner with time and this was attributed to the lack of temperature control which can be expected to change the response by several percent per degree centigrade. However, a careful examination of the data from one of the better runs (see Figures 3 and 4) indicates that a slight shift in the peak potential (probably a shift in the reference electrode potential or in the liquid-junction potential) had caused the real response peak to progressively shift between two measurement points and thus the apparent response changed. It is clear, therefore, that measurements should be spaced more closely on the potential axis. This will also make more feasible the application of smoothing on the potential axis, a process that had not been found helpful before. The penalty will be a slightly slower repetition rate and more data will be stored on the computer disk for each run

The primary factor limiting sweep-to-sweep reproducibility still seems to be flow control. Experimental results shows that the data in the potential region before reaching the stripping peak is much more reproducible than at the stripping peak. In the data set illustrating this report the standard error at 260 millivolts before the peak is only 1.76 AD levels while the peak showed 4.02 AD level noise. Averaging the top eleven points of the peak for each voltammogram still resulted in a standard error of 3.7 AD levels. This seems to indicate that the noise is not from the analog portions of the electronics or from the normal uncertainty in the digitization process (1/2 AD level).

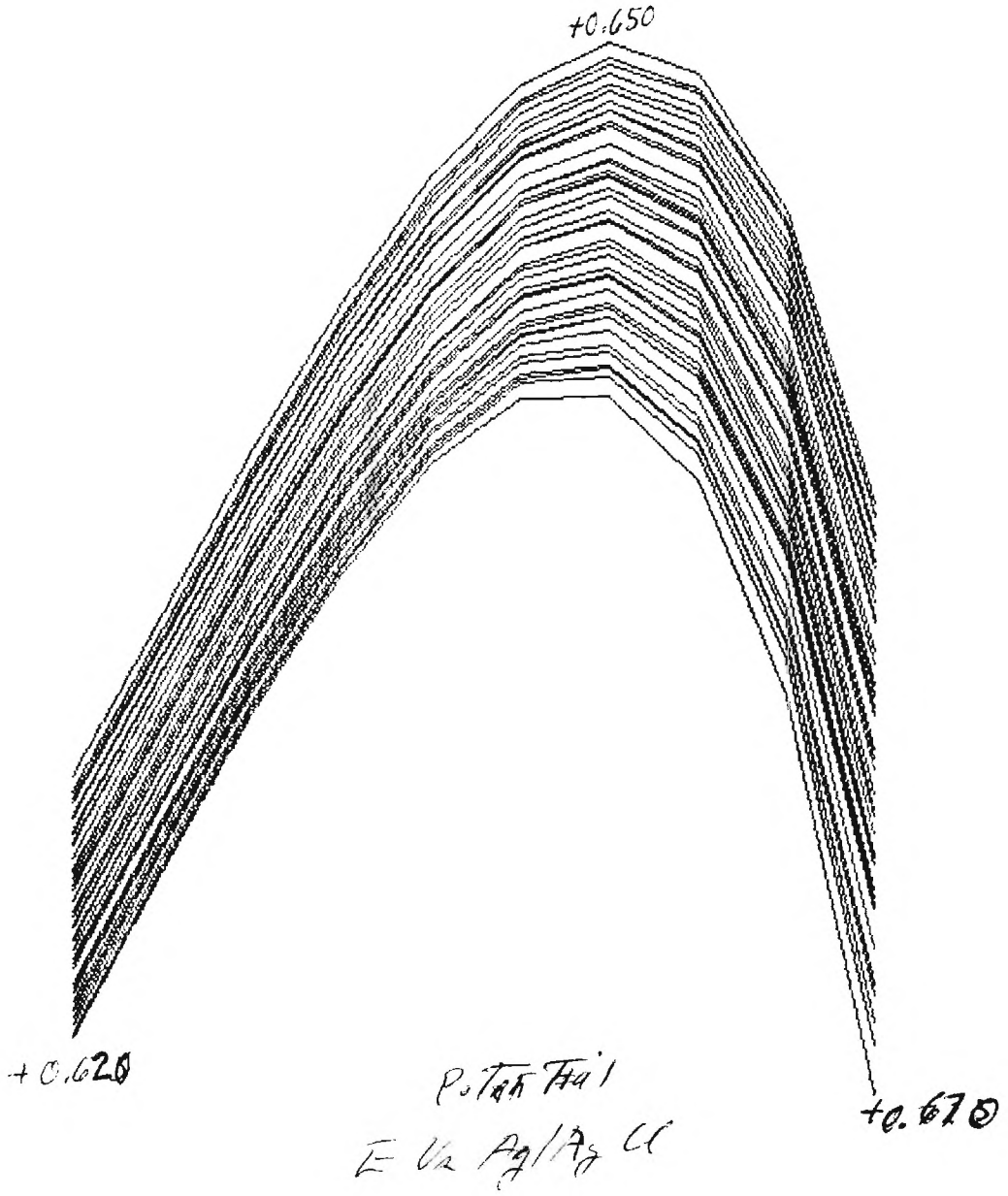

Figure 3. Detail of peak from Figure 2.

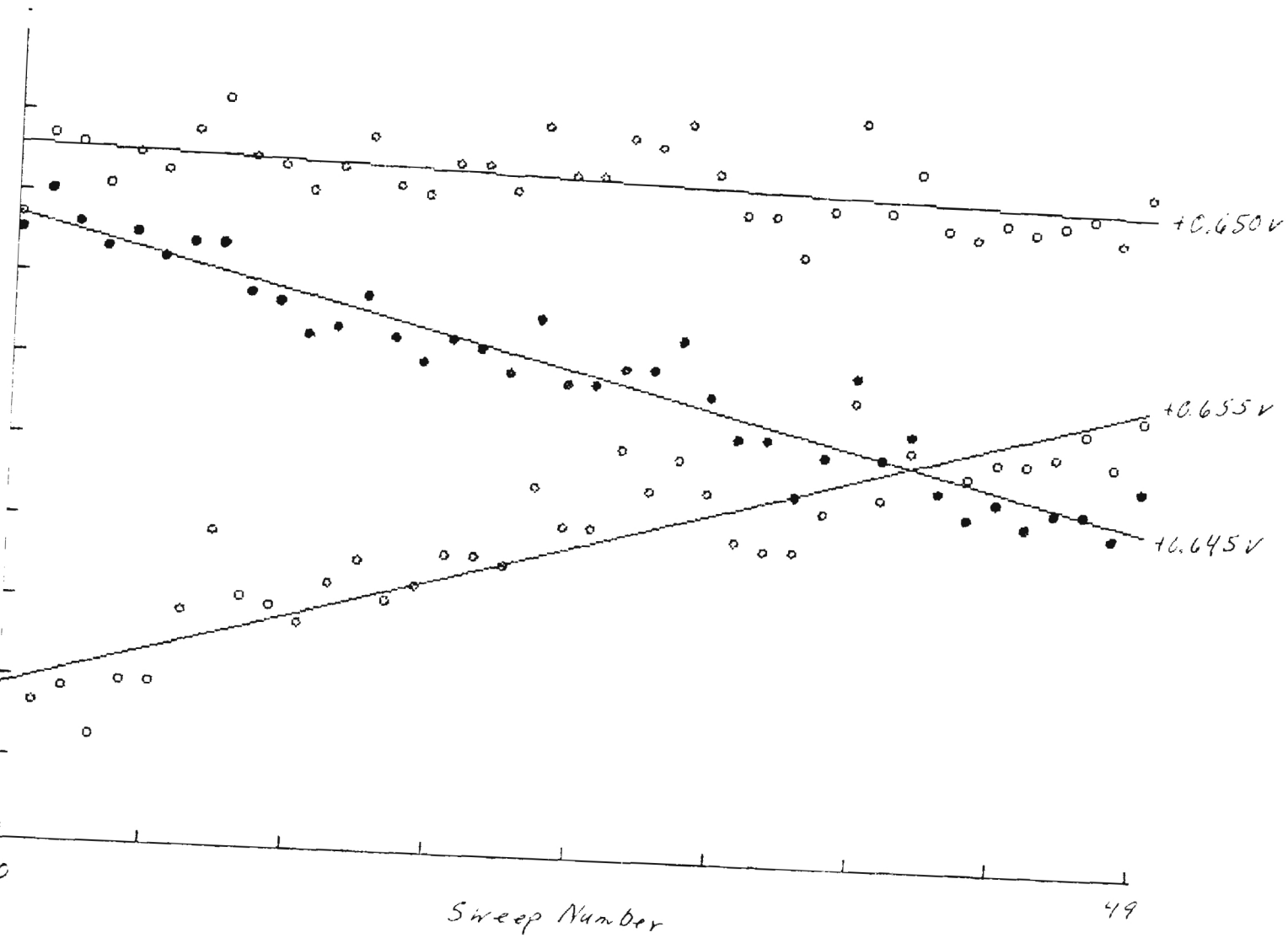

Figure 4. Regression lines from Figures 2 + 3.

Assuming that the primary limitation of sweep-to-sweep reproducibility is the pump, three possibilities are: variations of the bore of the pump cylinder, periodic binding and release of the piston seal, and irregularities in the screw drive of the piston. However, these possible sources should show an increase in frequency with increased flow rate, the opposite of the observed trend. A more likely source of the noise is a beat frequency between the stepper-motor frequency and the sampling frequency. These possibilities might be studied by monitoring the output of a high-quality pressure transducer. However, such an effort is not in the mainstream of this research and it is questionable that the results would be of any practical value. Another approach that might be helpful would be a new series of runs using the Haskel pump and the inline filter between the injector valve and the cell. This could be coupled to runs with more closely-spaced points as discussed above.

The experimental results reported here are for staircase stripping voltammetry, rather than square-wave stripping voltammetry as originally proposed. Experimental results showed that the voltammetric baseline was flatter for the square-wave technique, but that the baseline for staircase was acceptable. The deciding factor was that each point in a square-wave voltammogram is a difference measurement and thus the electronic noise and digitization errors would be expected to double for the square-wave technique.

At this time a complete determination has not been performed. This would require repetition of the measuring step with a series of carefully-prepared known solutions to establish a working curve and then using that curve to establish the concentration corresponding to the measurement on an unknown solution.

CONCLUSIONS

The work to date has demonstrated adequate sensitivity and marginally acceptable reproducibility. The primary limitations in reproducibility are thought to be in the pumping system and in the lack of temperature control. Some improvements in reproducibility can be expected through improvements in the apparatus and parameter optimization.

PROPOSED WORK

The PI believes that this project shows sufficient promise that important, fundamental questions can be answered and that the project should be continued for a second year to investigate these questions. Before the overall goals of the project can be achieved by any analytical technique, it must be established whether or not aluminum samples obtained from a Hall cell will be homogeneous enough to provide meaningful results. Thus it is important to make determinations on multiple aliquots of single aluminum samples obtain from a Hall cell which has been spiked with silver. After this has been answered satisfactorily, samples obtained from multiple points within a Hall cell, at the same time, should be analyzed to determine the spatial distribution and variability of concentration. If the results of these experiments show greater standard deviations than the analytical determinations of known standard solutions, it is doubtful that the ultimate goal can be attained by the silver-tracer approach. If, on the other hand, the results of these experiments are satisfactory, then a full test of the technique would be warranted. This would entail multipoint and multitime sampling from a producing Hall cell over a 24-hour period.

Before launching into the experiments proposed above, more technique development is indicated. First, the question of the best pump must be decided.

Some guidance can be obtained by using the Haskel pumps on hand. Then, either an ISCO syringe pump or a new Haskel pump equipped with a flow indicator must be procured. After that decision is made, a thermostated housing must be constructed for the entire apparatus. This housing must have sufficient space for temperature equilibration of multiple standard and sample solutions. It might be necessary to establish a data link from the present control computer to a more powerful host computer for data processing.

Another area of concern is the preparation of solutions. Examination of the table of tolerances for Class A volumetric glassware, indicates that serial, volumetric dilution would not be acceptable. At this time it appears that it will be necessary to calibrate volumetric flasks by weight and to transfer weight aliquots rather than volume aliquots. This will require the availability of high-quality balances which are not available in the School of Chemistry at Georgia Tech.